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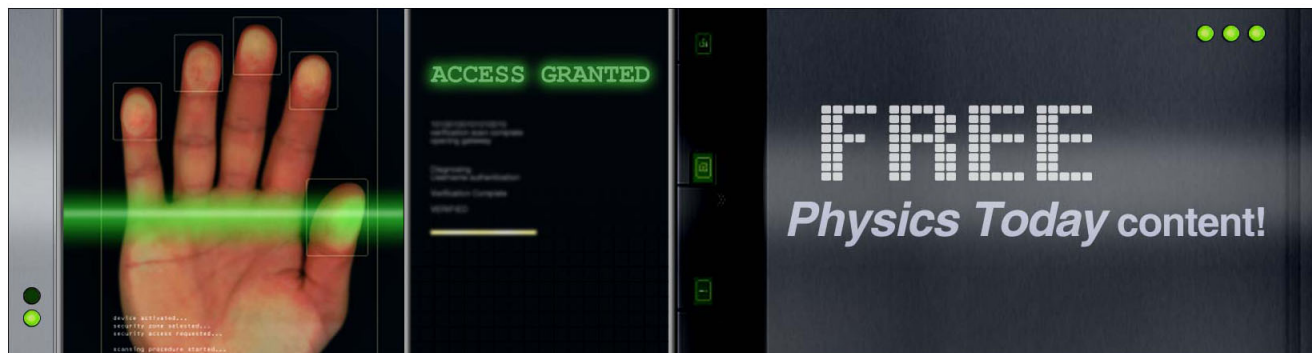
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Large magnetoresistances and non-Ohmic conductivity in $\text{EuWO}_{1+x}\text{N}_{2-x}$

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The magnetic field and voltage dependent electronic transport properties of $\text{EuWO}_{1+x}\text{N}_{2-x}$ ceramics are reported. Large negative magnetoresistances are observed at low temperatures, up to 70% in the least doped ($x=0.09$) material. Non-Ohmic conduction emerges below the 12 K Curie transition. This is attributed to a microstructure of ferromagnetic conducting and antiferromagnetic insulating regions resulting from small spatial fluctuations in the chemical doping. © 2009 American Institute of Physics. [DOI: 10.1063/1.3180813]

Materials in which the electrical current is coupled to magnetism or shows nonlinear variation with voltage are of fundamental interest and practical importance for technologies such as magnetoresistive random access memory¹ and resistive random access memory.² Many oxide families are known to have such properties, but the utility of an unexplored class of materials—europium(II) oxynitride perovskites—was recently demonstrated as colossal negative magnetoresistances (MRs) were discovered at low temperatures.³ The presence of nitride enables d^0 transition metals in high formal oxidation states to be stabilized, e.g., Nb,³ Ta,^{3,4} and W.⁵ Nitrogen-deficiency leads to electron-doping of the transition metal d -bands and the carrier transport may be strongly coupled to the magnetization from the Eu^{2+} $S=7/2$ core spins, leading to $-\text{MR}>99\%$ for $\text{EuNbO}_{2+x}\text{N}_{1-x}$ ($\text{MR}=[\rho(H)-\rho(0)]/\rho(0)$; ρ is resistivity, measured in zero field and magnetic field H). Here we report the magnetotransport properties of the correspondingly electron-doped material $\text{EuWO}_{1+x}\text{N}_{2-x}$, in which large negative MRs and microstructurally induced nonohmicity are discovered.

$\text{EuWO}_{1+x}\text{N}_{2-x}$ samples with $x=0.09$, 0.17, and 0.25 were prepared by ammonolysis of a precursor $\text{Eu}_2\text{W}_2\text{O}_9$, synthesized by heating Eu_2O_3 and WO_3 in air at 1100 °C for 72 h with intermediate regrinding. $\text{Eu}_2\text{W}_2\text{O}_9$ powder was nitrated at 800 °C during 15 h in flowing 99.9% NH_3 and quenched to room temperature under ammonia. N contents were controlled by varying the flow rate between 200 and 270 cm^3/min ; x decreases as the flow rate increases. 7 mm diameter pellets of the $\text{EuWO}_{1+x}\text{N}_{2-x}$ products for electrical measurements were pressed at 3 tons and subjected to a second ammonia treatment for 3 h under the same conditions. N contents were determined by combustion analysis.

The $\text{EuWO}_{1+x}\text{N}_{2-x}$ samples are single phase perovskites and appear cubic by powder x-ray diffraction [Fig. 1(a)] but electron diffraction revealed a body-centered $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ supercell as was also observed in EuNbO_2N .³ The cubic lattice parameter a_p increases slightly with the nitrogen deficiency x ($a_p=3.9592(4)$, $3.9622(2)$ and $3.9675(2)$ Å for $x=0.09$, 0.17, and 0.25, respectively) due to lattice expansion from electron doping into the W:5d band (reduction of W^{6+} to W^{5+}). The presence of Eu^{2+} , as found in the EuMO_2N

($M=\text{Nb}, \text{Ta}$) analogs,³ is confirmed by the mean Eu-O/N distances of 2.80–2.81 Å in these pseudocubic structures (cf. 2.88 and 2.68 Å, respectively, predicted from ionic radii of Eu^{2+} and Eu^{3+}) but full determinations of the superstructure will be needed to obtain accurate distances. Magnetization measurements show that the three samples order ferromagnetically at 12 K, as observed in a previous study of an $x=0.58$ sample,⁵ with no variation in T_C to within ± 0.5 K. Magnetization (M)—field (H) loops [Fig. 1(b)] confirm the ferromagnetic order although the saturated moment of $4.1\mu_B$ is significantly reduced from the theoretical value of $7\mu_B$ for Eu^{2+} , suggesting that spin canting or coexisting ferromagnetic and antiferromagnetic phases may be present, as discussed later.

The electronic transport properties of the three $\text{EuWO}_{1+x}\text{N}_{2-x}$ samples were measured using a Quantum Design physical properties measurement system down to 2 K and in fields up to 7 T, and a closed-cycle refrigerator operating down to 11 K. All resistivity measurements were carried out in the conventional four-point setup, where an ac current (I) of 0.5 mA was applied and the voltage (V) drop across the samples was registered. The resistivity of $\text{EuWO}_{1+x}\text{N}_{2-x}$ decreases with the electron-doping x and the temperature variations in Fig. 2(a) are typical for heavily

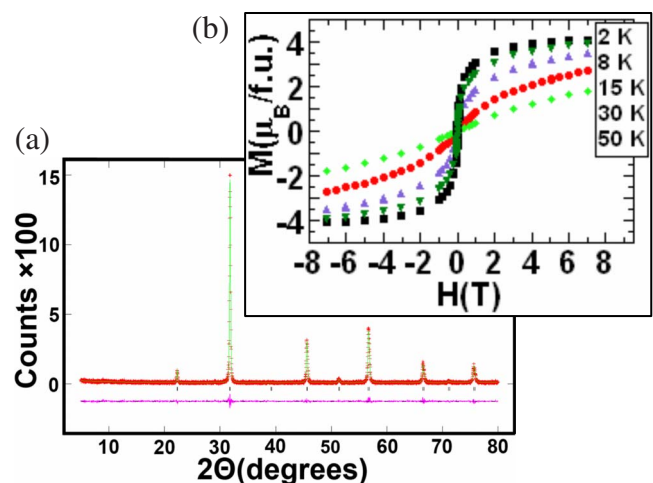


FIG. 1. (Color online) (a) Fit of a cubic perovskite model to the x-ray diffraction pattern and (b) magnetization-field loops, for $\text{EuWO}_{1+x}\text{N}_{2-x}$ ($x=0.17$ sample).

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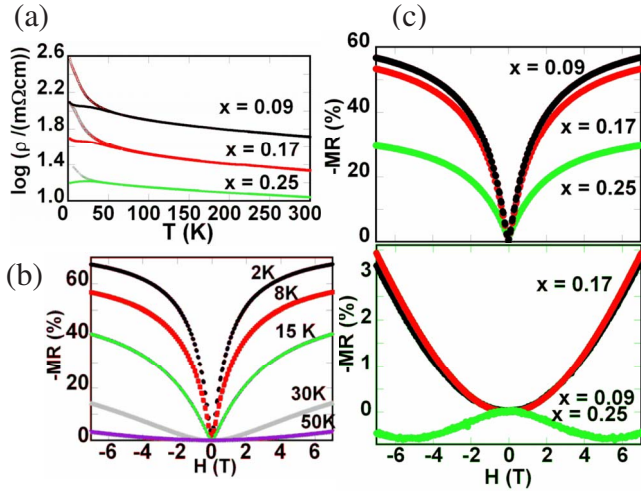


FIG. 2. (Color online) MR data for $\text{EuWO}_{1+x}\text{N}_{2-x}$ ceramics; (a) resistivities ρ for three samples in zero field (upper branch at low temperatures) and in a magnetic field of 7 T (lower branch at low temperatures), (b) $-\text{MR}$ vs field at temperatures of 2–50 K for the $x=0.09$ sample, (c) $-\text{MR}$ vs field for the three samples at 8 K (upper panel) and 50 K (lower panel).

doped semiconductors. Giant negative MRs are evidenced by the divergence of zero-field and in-field resistivities below ~ 50 K for $x=0.09$ and 0.17 and ~ 30 K for $x=0.25$ samples. This corresponds to the onset of ferromagnetic fluctuations as evidenced by the nonlinearity of $M-H$ below 50 K observed in Fig. 1(b) for $x=0.17$.

The field variation for the least doped ($x=0.09$) sample is shown in Fig. 2(b)—this displays the highest $-\text{MR} \approx 70\%$ at 2 K and 7 T. The thermal evolution of $-\text{MR}(H)$ follows an approximate $-\text{MR} \sim M^2$ relationship typical for lightly doped ferromagnetic insulators, so that $-\text{MR}$ changes from an H^2 dependence at 50 K in the paramagnetic region, to a sharp low field increase below T_C . Comparison of the MRs of the three samples in the ferromagnetic region [Fig. 2(c)] shows a decrease in the magnitude of $-\text{MR}$ with x as electron hopping becomes less coupled to the magnetization in the more conducting materials. The 50 K $-\text{MR}(H)$ curves in Fig. 2(c) show a different behavior between the $x=0.09$ and $x=0.17$ samples, which show virtually identical $\sim H^2$ dependences driven by ferromagnetic fluctuations, and the $x=0.25$ material in which the fluctuations are less pronounced and a small positive MR effect typical of paramagnetic semiconductors is observed.

During the magnetotransport measurements it became apparent that the three $\text{EuWO}_{1+x}\text{N}_{2-x}$ ceramics showed non-Ohmic conductivity at low temperatures and voltages. Systematic dc $I-V$ studies as a function of temperature were carried out in the 0–5 mA, 0–500 μV range to explore this nonohmicity. The effects are most pronounced for the $x=0.25$ sample, for which the $I-V$ isotherms are shown in Fig. 3. The $I-V$ behavior evolves from a linear, Ohmic relationship at high temperatures to the curve at 3 K, which changes from a Schottky (rectification) behavior at low V to an Ohmic variation at higher voltages. To explore the crossover we have fitted the isotherms down to 4 K as $I=AV^n+BV$, by varying the coefficients A and B and the exponent n . The temperature variation of n (Fig. 3 inset) captures the emergence of the Schottky term; the divergence of n above the ohmic $n=1$ limit coincides with the 12 K Curie transition. Hence, the ferromagnetic order drives the electrical change from ohmic to a nonlinear conducting regime in

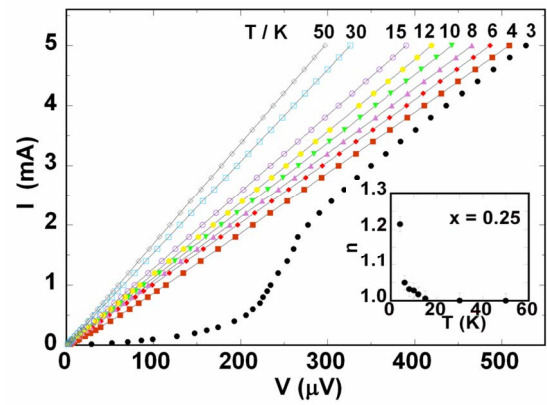


FIG. 3. (Color online) Current-voltage isotherms for the $x=0.25$ sample of $\text{EuWO}_{1+x}\text{N}_{2-x}$ at temperatures above (open symbols) and below (closed symbols) the 12 K Curie transition. Inset shows the thermal behavior of the exponent n from fitting the equation $I=AV^n+BV$ to isotherms at 4 K and above.

which both Schottky and Ohmic contributions are significant.

Non-Ohmic conduction arises from the presence of electrical inhomogeneities such as metallic and insulating regions which may be modeled as an appropriate arrangement of resistors and capacitors. For example, a composite of silver-coated glass spheres showed an $I=AV^n$ variation with $1 < n < 2$,⁶ and other models have been suggested for metal/semiconductor composite networks.^{7–9} Nonlinear conductivity was also observed in charge ordered manganite perovskites, and may be linked to the melting of charge order and creation of conducting filaments above a certain threshold current.^{10–12} This is qualitatively different to our findings where the nonlinear conduction occurs predominantly at low currents and appears to be intrinsically linked to the ferromagnetic ordering.

A likely explanation of the non-Ohmic behavior is that some regions within the $\text{EuWO}_{1+x}\text{N}_{2-x}$ samples are metallized below T_C . The effect is most pronounced in the most highly doped, $x=0.25$ sample, and accompanies a downturn (bulk metallic percolation) in the high field resistivity curve [Fig. 2(a)]. Small electrical inhomogeneities can arise from a slightly inhomogeneous O/N (doping) distribution created during the sintering of the ceramic pellets, although this does not usually give rise to such pronounced nonohmicity. We propose that the effect of this slight inhomogeneity is amplified by the low temperature magnetic order in $\text{EuWO}_{1+x}\text{N}_{2-x}$. The saturated moment of $4.1\mu_B$ [Fig. 1(b)] has only 60% of the expected value, showing that substantial canting or segregation into ferro- and antiferromagnetic phases occurs. The latter picture is supported by the properties of the related material EuTiO_3 , which is antiferromagnetic in zero field but shows a field-induced ferromagnetism.¹³ Small compositional fluctuations in $\text{EuWO}_{1+x}\text{N}_{2-x}$ lead to spatial variations in the ferromagnetic order parameter, resulting a microstructure of ferromagnetic metallic and insulating antiferromagnetic regions that conducts nonohmically. This microstructure is also sensitive to the electric field; high voltages further metallize the sample and Ohmic behavior is recovered, as observed in the 3 K isotherm on Fig. 3.

To conclude, $\text{EuWO}_{1+x}\text{N}_{2-x}$ ceramics displays large negative MRs and magnetically driven nonohmicity at low temperatures. The MR results from coupling of the doped W

d-band carriers to the Eu^{2+} magnetization, and so is sensitive to the doping, field and temperature. Non-Ohmic behavior emerges from spatial fluctuations in the ferromagnetic order that create a microstructure of insulating and conducting regions. Manipulation of the O/N content within $\text{EuWO}_{1+x}\text{N}_{2-x}$ films or monoliths could thus be used to create spintronic or nonlinear resistive devices operating at low temperatures.

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